# ESTCP
Cost and Performance Report

(ER-201121)
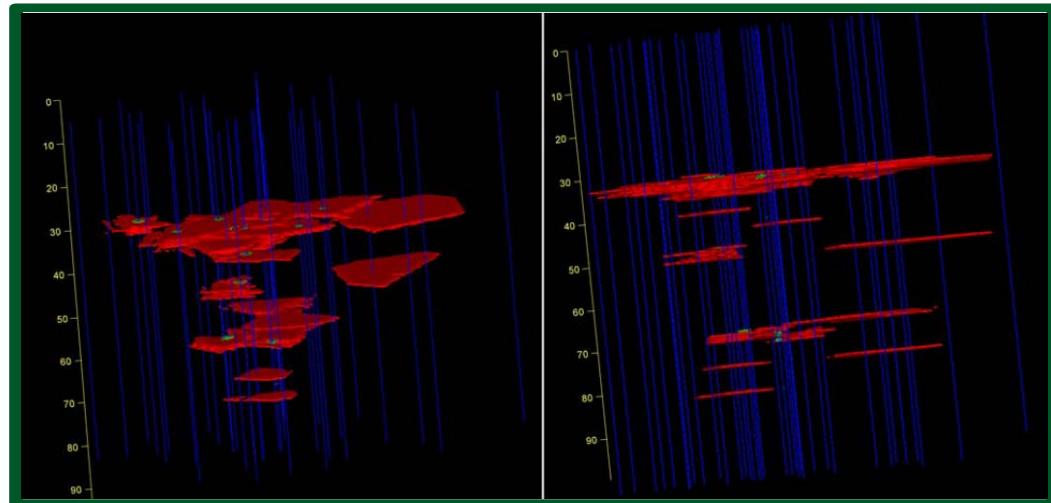
Direct Push Optical Screening Tool for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture

July 2016

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ESTCP

ENVIRONMENTAL SECURITY
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COST & PERFORMANCE REPORT
Project: ER-201121

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ACRONYMS AND ABBREVIATIONS

3D	Three-Dimensional
ADA	Advanced Data Analysis
APS™	Advanced Profiling System
ATSM	American Society for Testing and Materials
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
cm	centimeter
CPT	Cone Penetrometer Testing
CSM	Conceptual Site Model
Dakota	Dakota Technologies, Inc.
DNAPL	dense non-aqueous phase liquid
DP	Direct Push
DSITMS	Direct Sampling Ion Trap Mass Spectrometer
DyeLIF™	Dye-Enhanced Laser-Induced Fluorescence
ESTCP	Environmental Security Technology Certification Program
HPT™	Hydraulic Profiling Tool
HRSC	High Resolution Site Characterization
LIF	Laser Induced Fluorescence
MGP	Manufactured Gas Plant
MIP	Membrane Interface Probe
mL	milliliter
mm	millimeter
NAPL	non-aqueous phase liquid
PAH	Polycyclic Aromatic Hydrocarbon
PID	Photoionization Detector
sec	second
TarGOST®	Tar-specific Green Optical Screening Tool
UVOST®	Ultra Violet Optical Screening Tool
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

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ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

This Cost and Performance Report describes field testing of a new direct push (DP) optical screening tool: A high-resolution three-dimensional (3D) subsurface mapping of chlorinated solvent dense non-aqueous phase liquids (DNAPLs) in un-lithified sediments. The new tool, a laser induced fluorescence (LIF) technology referred to as Dye-Enhanced Laser-Induced Fluorescence (DyeLIF™,) was developed and validated during this Environmental Security Technology Certification Program (ESTCP) project. It is now commercially available from Dakota Technologies,Inc.(Dakota)[1].

The DyeLIF tool is a new site characterization technology that— for the first time— facilitates rapid, cost-effective, (3D) delineation of residual chlorinated solvent DNAPL in the subsurface (**Figure ES-1** below). This type of high-resolution source characterization can identify previously unknown residual DNAPL, thereby optimizing source zone excavation or in situ treatment programs. In particular, high-resolution characterization using DyeLIF can dramatically reduce cumulative remediation costs and improve remediation performance by targeting excavation or treatment on the most impacted areas that convey mass to potential receptors. Similarly, a site investigations program using DyeLIF can also quickly determine that residual DNAPL is not present in the subsurface at a particular site. This knowledge can also be very valuable for risk evaluations and scoping of remediation systems.
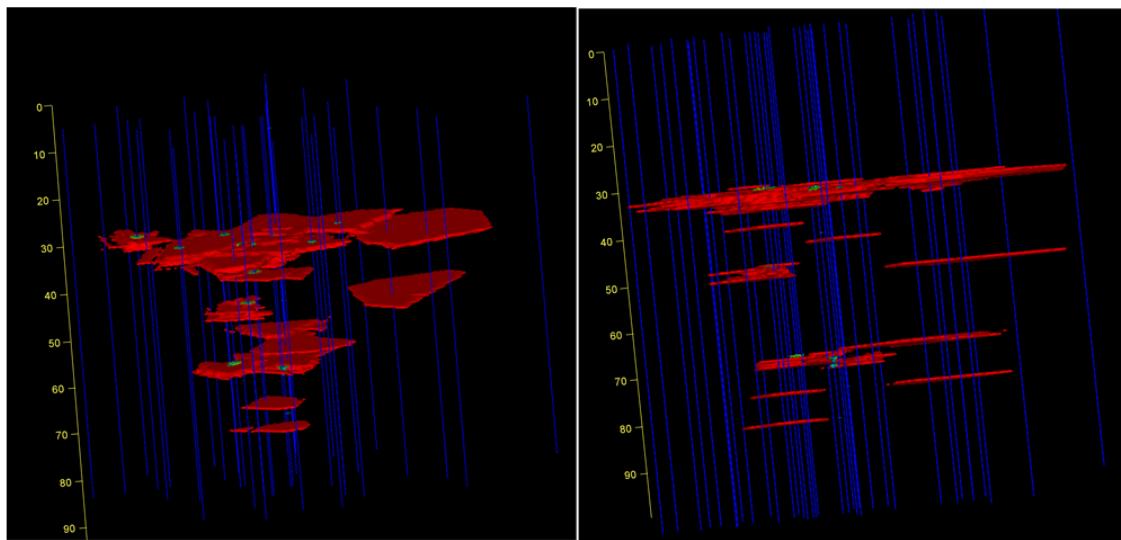
Figure ES-1. 3D Graphical Depictions of the DNAPL Source Zone at Demonstration Site.

This site assessment, performed in only four days using DyeLIF, provides the most detailed delineation of subsurface DNAPL ever made at a non-research field site.

In addition to yielding information on the subsurface DNAPL distribution, the recording of dye solution, flow rate, and injection back-pressure provides high-resolution information on the lithology and hydraulic conductivity of the soil, similar to other profiling tools such as the Geoprobe® HPT™ (Hydraulic Profiling Tool) and Waterloo APS™ (Advanced Profiling System).

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[1] [http://www.dakotatechnologies.com/services/dyelif]

The DyeLIF system was field tested at a Formerly Used Defense (FUD) facility in Massachusetts, in Fall 2013 (Geoprobe delivery) and again in March 2014 (cone penetrometer testing [CPT]™ delivery). The primary field demonstration completed in 2013 included two components: one week of DyeLIF probing and a second week of follow-on soil coring, Using research-quality DP soil coring methods to compare DyeLIF results to colorimetric dye shake tests and laboratory analysis.

Several performance objectives were established in the project demonstration work plan, and all were met or exceeded. The performance objective for chemical analysis was 70% consistency between positive DyeLIF responses and samples where DNAPL saturations were > 5%. The demonstration results showed 100% consistency between chemical analysis and DyeLIF for saturations > 1.9% (35 of 35 samples), and 95% consistency for estimated saturations > 0.5% (40 of 42 samples).

The performance objective for the dye shake tests was 70% consistency between a positive DyeLIF response and a positive colorimetric response with the dye shake test when the DNAPL saturation was estimated to be > 5%. For the dye shake tests, the demonstration results showed 100% consistency between DyeLIF and the shake tests at saturations as low as 1.3% (37 of 37 samples). There was 98% consistency between DyeLIF and dye shake tests > 0.5% saturation (41 of 42 samples). Therefore, the performance objective for dye shake tests was also exceeded.

The hammering and stress of percussive drilling over the one week drilling program allowed the project team to evaluate the durability of the DyeLIF tool. A performance objective of 90% uptime was specified in the work plan for the field demonstration, which was achieved by 100% uptime. A performance objective was also established for the average linear feet of drilling production achieved per day. A performance goal of 150 feet per day was proposed in the work plan. The production rate for the week of DyeLIF probing averaged over 400 feet of probing per day, greatly exceeding the 150 feet per day goal. The production rate, coupled with the extremely fine vertical resolution of DyeLIF (~ 1 data point per 0.5 centimeters probed) results in an extremely high data acquisition rate for the DyeLIF tool. Using a typical LIF production rate average of 334 feet probed per day,2 the number of data points generated per day would be greater than 20,000. Considering the excellent correlation between DyeLIF and colorimetric dye shake tests, one day of DyeLIF probing is essentially equivalent to conducting 20,000 colorimetric dye shake tests. Something similar to that would take several months of expensive soil coring and detailed sub-coring to complete.

A detailed cost comparison is included. It compares DyeLIF to high-resolution soil sampling. Another cost that is important to consider is the benefit that DyeLIF could have on remediation costs and performance. More accurate mapping of DNAPL source zones allows for more targeted and focused source zone remediation, particularly if in-situ remedial options or excavation are selected.

The Final Report also includes recommendations and strategies for using the DyeLIF tool for DNAPL source zone investigations. The complimentary nature of other high resolution site characterization (HRSC) to the DyeLIF tool is also discussed.

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2 Dakota Technologies Inc. has maintained a running average production rate for its TarGOST® LIF tool over many years and dozens of sites probed. That average is 334 feet per day.

1.0   INTRODUCTION

This Cost and Performance Report summarizes the field testing of a new direct push (DP) optical screening tool for high-resolution subsurface mapping of chlorinated solvent dense non-aqueous phase liquids (DNAPLs) in un-lithified sediments. The new tool, referred to as dye-enhanced later-induced fluorescence (DyeLIF™), was developed and validated during this environmental security technology certification program (ESTCP) project and is now commercially available from Dakota Technologies, Inc. (Dakota).[3] Additional details on this ESTCP project can be found in the Final Report.

1.1   BACKGROUND

Chlorinated solvents are among the most common organic contaminants detected in groundwater at U.S. Department of Defense (DoD) sites. The sources of these dissolved contaminants are often historical releases of DNAPLs. The distribution of residual DNAPL is typically complex due to small-scale variations in soil permeability (Kueper et al., 1993) and to the 'aging' of the DNAPL source zones during the years to decades since the initial DNAPL releases occurred. During that time, dissolution accentuates the heterogeneous distribution of chlorinated solvent DNAPLs, making it even more difficult to locate the residual DNAPL (Guilbeault et al., 2005; Parker et al., 2003).

Until the development of the new DyeLIF technology, no field methods have existed for rapidly delineating subsurface DNAPL in three-dimensions (3D). The Final Report includes a detailed review of field methods that have historically been used to investigate DNAPL sites. One high resolution site characterization (HRSC) tool discussed in the Final Report was the Membrane Interface Probe (MIP). MIP is a common DP sensor used at sites where chlorinated solvents have been released. The MIP can be advanced using a Geoprobe® or cone penetrometer testing (CPT) rig (Christy, 1996). The downhole portion of the tool consists of a heated membrane that allows volatile organic compounds (VOCs) in the soil adjacent to the membrane to volatilize and diffuse across the membrane and into a carrier gas. The carrier gas is routed to a series of aboveground detectors that provide semi-quantitative information on the concentration and type of VOCs in the vicinity of the membrane. A significant limitation of the MIP tool for non-aqueous phase liquid (NAPL) source zone investigations is that it is unable to differentiate high-concentration dissolved and vapor-phase contamination from NAPL (McAndrews et al., 2003; Ravella et al., 2007). This limitation is particularly important when high-strength dissolved plumes exist downgradient of NAPL source zones. Because of the heterogeneity of the NAPL source zones, most of the dissolved-phase contamination is migrating away from the source zone. The contamination is typically concentrated in a number of high-concentration but small cross-sectional-area plume 'cores' or 'local maxima' (Guilbeault et al., 2005). Those plume cores, which may only comprise 1015% of the cross-sectional area of the plume, commonly convey 70– 80% of the contaminant mass flux at DNAPL sites (Guilbeault et al., 2005). Early conceptualizations of dissolved phase plumes, however, predicted that there would be significant homogenization and mixing as contaminants migrated downgradient from the DNAPL source. Studies that have employed high-resolution characterization of the dissolved-phase plume along one or more transects oriented perpendicular to the groundwater flow direction.

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[3] [http://www.dakotatechnologies.com/services/dyelif]

However, that hydrodynamic dispersion (mixing) is much less than was originally thought and high concentration plume cores can maintain their strength and structure over relatively long travel distances (Einarson et al., 2010). The significance of this in relation to characterization of DNAPL source zones with MIP is that high-strength plumes may be misidentified as areas of residual DNAPL using technologies like MIP. Also, carryover (lingering VOCs within the sampling tubing and fittings) often creates a positive bias with MIP, particularly when penetrating DNAPL zones, which can give the impression of a much thicker and deeper NAPL zone than is actually present (Bumberger et al., 2012).

In contrast to MIP technologies, Laser Induced Fluorescence (LIF) technologies respond only to NAPL and consequently there is no chance of mistaking a high-concentration dissolved plume core for a NAPL source zone. In other words, LIF is specific to NAPLs and does not respond to absorbed, dissolved, or vapor (gas) phase VOCs. This is a key advantage of LIF tools over MIP for accurate delineation of NAPL source zones. Furthermore, LIF tools also have extremely high vertical resolution (centimeter [cm] scale) and probing rates typically exceed 300 linear feet per day. This high vertical resolution coupled with typical probing production rates translates into tens of thousands of data points generated per day. High data production rates make LIF tools very cost-effective for characterizing NAPL source zones in 3D, which requires a large quantity of data due to the inherent highly heterogeneous nature of most DNAPL source zones. LIF tools also provide data in real time, similar to other direct sensing equipment, which allows for the use of dynamic (adaptive) work plans where subsequent probing locations are selected in the field as new data is acquired.

The foundation of LIF technologies is historically used in subsurface environmental assessments it i the natural fluorescence of polycyclic aromatic hydrocarbons (PAHs) found in the NAPLs being investigated. As the probe rods are advanced into the subsurface using DP rigs (e.g., Geoprobe, CPT), pulses of light are emitted through a small sapphire window present near the base of the probe rod. The emitted light, which is otherwise reflected (or scattered) by soil, is absorbed by PAHs such as those found in petroleum hydrocarbon and manufactured gas plant (MGP) tar NAPLs. The excited-state PAHs quickly yield fluorescence, which is transmitted to the ground surface via optical fibers in the probe rod, where it is analyzed in real-time using optical data processing equipment located in the DP rig.

The requirement that the NAPL being investigated contain PAHs for detection has up until now limited the usage of LIF to sites impacted by petroleum hydrocarbon fuels, creosotes, and MGP tars. The rapid, high-resolution, real-time nature of LIF technologies described above has revolutionized NAPL source zone investigations at those types of sites. However, conventional LIF tools to this point have generally not been able to detect chlorinated solvent DNAPLs because chlorinated solvents lack the PAH compounds responsible for the laser-induced fluorescence in coal tars and petroleum hydrocarbons.[4] To extend the LIF technology to chlorinated solvent DNAPLs, a new tool, referred to as the DyeLIF optical screening tool, was developed and field tested, the results of which are described in this report.

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[4] Sometimes chlorinated solvents can have a high amount of PAH-containing materials that solvated in them, which makes them detectable with conventional LIF technologies. There is no response of LIF to pure chlorinated solvent as they lack the aromatic ring structure that causes fluorescence.

The primary modification made to existing LIF technology to allow for detection of chlorinated DNAPL was to add a small dye injection port beneath the sapphire window in the probe rods. As the DyeLIF probe is advanced into the subsurface, a steady stream of hydrophobic fluorescent dye is injected. If DNAPL is present adjacent to the probe rod, the dye partitions into the DNAPL, causing the solvent DNAPL to fluoresce once excited by the LIF laser. The dye therefore circumvents the requirement that the DNAPL contain naturally fluorescing PAHs. The continuous injection of an aqueous dye solution as the tool is advanced also allows for detailed vertical profiling of soil permeability.

1.2   OBJECTIVE OF THE DEMONSTRATION

The objective of the field demonstration was to provide a field-scale demonstration of the new DyeLIF tool for high-resolution subsurface mapping of chlorinated DNAPLs. The real-time, high-resolution profiles generated from the DyeLIF were then compared to profiles from high-resolution vertical soil sampling with subsequent dye shake tests and quantitative laboratory VOC analysis.

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2.0   TECHNOLOGY

2.1   TECHNOLOGY DESCRIPTION

Existing, commercially-available LIF technologies such as Dakota's Ultra-Violet Optical Screening Tool (UVOST®) and the Tar-specific Green Optical Screening Tool (TarGOST®) are popular tools for real-time, high-resolution mapping of petroleum hydrocarbons, creosotes, and coal tar-based NAPLs for sites with subsurface conditions amenable for DP probing techniques[5]. Existing LIF technologies are described below, followed by a discussion of the new DyeLIF tool, which is the focus of this ESTCP project.

While DyeLIF is based upon these existing LIF technologies, several important system modifications were made in order to lower the level of detection limit (i.e., the lowest NAPL saturation that can be detected) and increase the spatial resolution of data points (currently one data point for every 0.4–0.5 cm probed). The project team anticipates that chlorinated solvent DNAPL at many sites will have more complex architectures and be present at lower saturations and in thinner layers than MGP tar, creosote, and petroleum hydrocarbon fuels due to higher densities, lower viscosities, and increased weathering (mass depletion) of residual chlorinated solvent DNAPL. The current, optimized version of DyeLIF is described further below and is now commercially available from Dakota[6].

Existing LIF tooling (e.g., UVOST, TarGOST) is advanced in the subsurface using CPT and percussion DP systems such as Geoprobe. The tools consist of a light source (laser), fiber optics strung through the rod string, with optical detection and processing equipment. As the probe rods are advanced into the subsurface, short duration (1–2 nanoseconds) pulses of excitation light are emitted through a sapphire window present near the probe's tip or above the tip and sleeve sensors in the case of CPT. The light from the laser is then emitted from the window where it is absorbed or reflected (scattered) by soil or is absorbed by any PAHs found in the petroleum hydrocarbon, coal tar, or creosote NAPLs. The excited state of the PAHs quickly yield fluorescence, some of which travels back inside the probe where it is captured and transmitted back to the ground surface via an optical fiber, where it is analyzed in real-time using detectors and data processing equipment located at the surface.

Unfortunately, the LIF tools described above do not work with chlorinated solvent DNAPLs because chlorinated solvents lack the aromatic structure responsible for fluorescence (like that of PAHs). To extend existing LIF technology to NAPLs that do not contain PAHs, a new LIF technology has been developed. The new LIF optical screening tool DyeLIF works by injecting an emulsion containing particles of fluorescent, hydrophobic dye through a small injection port located 22 cm below the sapphire window as the probe is advanced through the subsurface. The injected dye dissolves into the NAPL (if present) and fluoresces in the presence of a light source, allowing the same LIF tooling (lasers, optical reading, and processing equipment) to be used to detect chlorinated solvent DNAPLs. This allows for chlorinated solvent DNAPL source zones to now be mapped using the same real-time, high-resolution techniques that have historically been available only for petroleum hydrocarbon-and coal tar-based NAPLs.

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[5] [http://www.dakotatechnologies.com/home]
[6] [http://www.dakotatechnologies.com/services/dyelif]

In addition, it is anticipated that the new LIF tool will be useful for boosting the ability to detect PAH-poor petroleum hydrocarbon NAPLs such as aviation gasoline and single-ring aromatic compounds like benzene, toluene, ethylbenzene, and xylenes (BTEX).

DyeLIF is a modified version of Dakota's TarGOST tool, which is used for creosote and MGP tar detection. A schematic of the downhole tooling for percussion DP system deployment (e.g., Geoprobe) is shown in **Figure 1**. The probe functions by injecting an emulsion of distilled water and particles of a proprietary hydrophobic dye through a small injection port that is situated 22 cm below the LIF sapphire window. As the probe is advanced through the subsurface, the injected emulsion deposits a film of indicator dye along the side of the probe in order to create an "interaction zone" where the dye will partition into DNAPL if it is present in the soil. Standard LIF instruments are then used to detect the fluorescence generated by the dye-labeled chlorinated solvent DNAPLs.
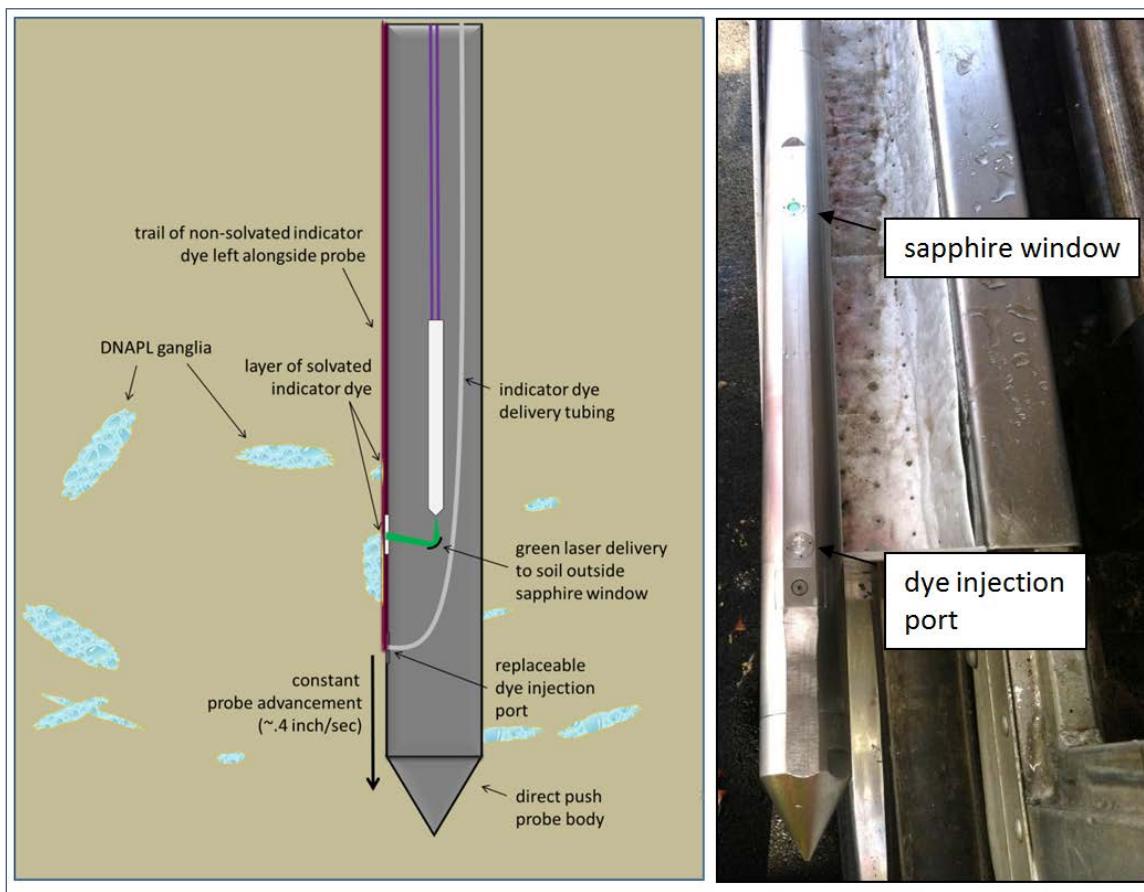
Figure 1. DyeLIF Probe Schematic (Left) and Field Photo of Percussion-Delivered Version (Right).

A version of the DyeLIF that is compatible with CPT has also been developed and is shown below in **Figure 2**. The LIF detection system's sapphire window and the injection port dimensions and their relative geometry on the CPT DP system is nearly identical to the percussion DP tooling in an effort to maximize similarity between the two different delivery platforms.
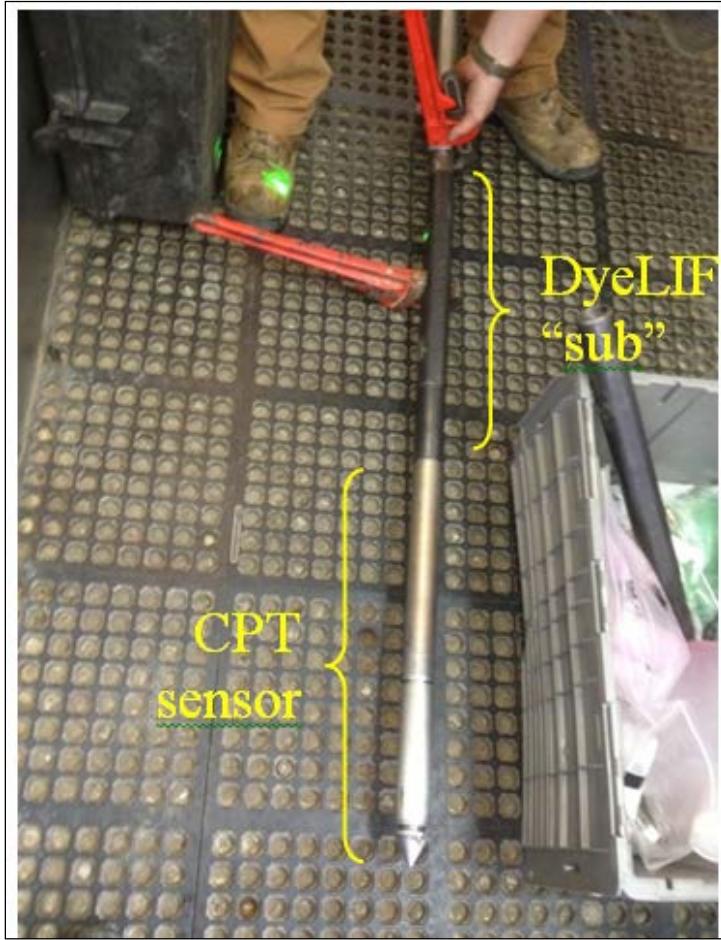
Figure 2. CPT Delivered Version of DyeLIF.

The solvation of the dye from its emulsion into the DNAPL takes just milliseconds to occur, allowing for a continuous advancement of the DyeLIF probe as opposed to other direct sensing equipment that requires stops at specified depth intervals while measurements are taken. Penetration rates of about 1.0 cm/sec (slightly below the American Society for Testing and Materials [ASTM] CPT range of 1.5–2.5 cm/sec) have been used to date in order to maximize the detection of thin cm-scale NAPL layers. Penetration rates control data density because the DyeLIF system acquires data at a fixed rate based on laser pulses, rather than distance. At a 1.0 cm/sec advancement rate, the average data spacing is 0.4–0.5 cm. A significant change of performance at higher probe advancement speeds is not expected other than an increase in data spacing and an accompanying "averaging out" of small, but potentially important responses potentially causing non-detects in such intervals. This sub-centimeter scale resolution is preferable as previous high-resolution soil sampling of DNAPL source zones has found that DNAPL typically occurs in zones with one or more thin layers, commonly between 1 and 30 cm in thickness (Parker et al., 2003).

The dye is injected at a target flow rate of 1 milliliter per second (mL/sec), which works out to approximately 0.11 grams of dye for each meter of penetration (assuming 1 cm/sec advancement rate). These low fluid injection rates minimize the risk of displacing DNAPL ganglia away from the probe rod and outside DyeLIF's zone of optical interrogation.

In addition to yielding information on the subsurface DNAPL distribution, the dye solution injection rate and back-pressure is measured and recorded. This provides high-resolution information on the lithology and hydraulic conductivity of the soil, similar to other profiling tools such as the Geoprobe HPT™ (Hydraulic Profiling Tool) and Waterloo APS™ (Advanced Profiling System). The dye solution flow rate and back pressure are continuously monitored by pressure and flow sensors and logged by the Optical Screening Tool software that logs the fluorescence response. The resulting DyeLIF logs portray corresponding depth profiles of fluorescence response (DNAPL indicator), dye solution flow rate, and dye-solution back-pressure. Since DNAPL often pools and spreads laterally when permeability contrasts are encountered, the soil permeability information provides important supplementary information on soil type/permeability. For example, at this ESTCP project's demonstration site, a fluorescence response indicates DNAPL was present in a more permeable zone overlying a lower permeability unit or layer, consistent with conceptual models of DNAPL migration in stratified formations.

2.1   ADVANTAGES AND LIMITATIONS OF TECHNOLOGY

As described above, the sensitivity of migrating DNAPL to small-scale changes in soil permeability often leads to complex distributions of DNAPL in the subsurface (DNAPL architecture). Accurate delineation of the DNAPL location and distribution, therefore, necessitates collection of a large quantity of data in order to thoroughly define the DNAPL both laterally and vertically. Traditional coring-based methods like soil sampling and dye shake tests may provide accurate point-scale information at relatively few locations, but are limited in terms of the amount of data that can be generated for a given investigation budget. LIF tools offer significant advantages compared to conventional approaches because they quickly provide high-resolution, real-time information about the distribution of NAPL in the subsurface. Most importantly, LIF tools produce a significantly larger amount of data for the same amount of money spent using conventional approaches. Specific advantages of the DyeLIF include:

- **High data acquisition/production rates** – A large number of data points are typically needed to adequately characterize DNAPL source zones. The DyeLIF tool produces tens of thousands of data points per day (typically > 20,000 data points per day) making the tool much more cost effective than conventional approaches (e.g., soil coring and sampling).

- **High vertical resolution** – High resolution, research-level soil sampling investigations of chlorinated solvent DNAPL source zones have indicated that DNAPL typically occurs in one or more very thin layers ranging in thickness from 1 to 30 cm (Parker et al., 2003). The vertical resolution of the DyeLIF is 0.4 to 0.5 cm, making it sensitive enough to detect even sub-cm thick layers of DNAPL.

- **Real-time data acquisition** – Dynamic work plans, where investigation locations are selected in the field based on real-time data acquisition, are essential for effective DNAPL investigations. Real-time data acquisition allows for DNAPL source zones to be completely delineated in a single mobilization.

- **Differentiation between NAPL and dissolved phase contamination** – As described above, MIP is capable of real-time, high-resolution mapping of subsurface VOCs but cannot differentiate between dissolved/absorbed phase contamination and DNAPL.

The inability to differentiate a high-strength dissolved mass from DNAPL limits the utility of the MIP tool for determining the location of DNAPL in source zones. The footprint of the presumed DNAPL source zone can appear much larger with MIP data than it actually is.

The primary limitation of the LIF technology is that it is semi-quantitative and does not provide detailed information regarding DNAPL composition and saturation as it can be obtained via analysis of soil samples at a fixed laboratory. DyeLIF can, however, quickly delineate the locations of residual DNAPL in the subsurface. Selective soil sampling can then be performed, targeting specific DNAPL zones for chemical analysis.

The semi-quantitative nature of DyeLIF is similar to other HRSC technologies such as MIP. More quantitative information about a single point in space is traded for semi-quantitative information for a much larger number of data points providing much greater spatial resolution. HRSC techniques have stimulated their own increased usage as they have demonstrated just how complex most sites are, both in terms of geology and contaminant distribution. This increased understanding of system complexity has in turn led to more usage of HRSC as these technologies provide data at the spatial resolution and data production rates required to effectively characterize and remediate these sites. Trying to develop Conceptual Site Models (CSMs) from a limited monitoring well network and conventional soil sampling is simply not effective for complex chlorinated solvent sites. These sites require the use of HRSC techniques in order to develop accurate CSMs and effective remediation strategies. Selective and targeted soil sampling at key locations selected based on the HRSC dataset can provide a basis for better understanding and approximate calibration of the DyeLIF response.

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3.0 PERFORMANCE OBJECTIVES

Quantitative performance objectives were based on comparisons of three different analyses of sub-cores collected from the same cores at the same depths. The three analyses were (1) quantitative analysis of soil at a fixed laboratory, (2) analysis using conventional field-based colorimetric dye "shake tests" using Oil-Red-O dye, and (3) a "tabletop" application of DyeLIF whereby the DyeLIF probe was placed horizontally on a bench and then soil sub-cores in 25 mL glass vials with the DyeLIF solution were passed in front of the sapphire window on the DyeLIF probe to measure the LIF response.

In this way, all three tests were conducted on sub-samples from the same core at the same depth interval in order to minimize uncertainty from incomplete core recovery, spatial variability, etc. Qualitative performance objectives also included tool durability and production rates (e.g., how many linear feet can be advanced per day). The performance objectives are summarized in **Table 1**.

Table 1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Correlation of DyeLIF with quantitative chemical sampling	Piston core barrels, split on their vertical axis for sub-coring purposes and quantitative lab analysis	70% consistency between DyeLIF and chemical analysis for samples > 5% DNAPL saturation[1]	100% consistency > 1.9% saturation (n = 35). 95% consistency (40 of 42 samples) > 0.5% saturation.
Correlation of DyeLIF with qualitative dye shake tests	Piston core barrels, split on their vertical axis for sub-coring purposes. Sub-cores analyzed with dye shake test for qualitative presence/absence of DNAPL.	70% consistency between DyeLIF and dye shake test for samples above 5% DNAPL saturation[1]	100% consistency > 1.3% saturation (n = 37). 98% consistency (41 of 42 samples) > 0.5% saturation.
Qualitative Performance Objectives			
Durability	Week long probing event to put stress on equipment	> 90% uptime.	100% uptime by rotating two DyeLIF setups (same approach used by most MIP vendors)
Production rates	Week long probing event	> 150 feet of probing per day	DyeLIF averaged > 400 feet of probing per day[2]
No drag-down of DNAPL	DyeLIF response signal; detailed coring used for quantitative performance objectives	Rapid drop-off in DyeLIF signal below DNAPL layers (see Figure 2); same rapid drop-off in co-located soil core subsamples	No evidence of drag-down or vertical mobilization in any DyeLIF logs or soil borings.

Notes: 1. DNAPL saturations estimated by converting chemical concentration to estimated DNAPL saturation using NAPLANAL software, which is based on equilibrium partitioning theory.

2. Production rate was helped by a second rig on-site that was performing re-entry grouting. This approach prevented any downtime of the DyeLIF rig during grouting. It is estimate that the production rate would have decreased approximately 25% if the DyeLIF rig performed the re-entry grouting.

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4.0   DEMONSTRATION SITE DESCRIPTION

4.1   SITE LOCATION AND HISTORY

The site is a former ordinance plant located in Lowell, Massachusetts (Site). The area where the demonstration occurred was an active DNAPL recovery area that constitutes only a small portion of the overall Site (see inset map in **Figure 3**). DNAPL recovery in the demonstration area has been ongoing since February 2007. A series of recovery wells were installed in the demonstration area between 2007and 2009. The nature of historical operations responsible for the DNAPL releases is unknown.
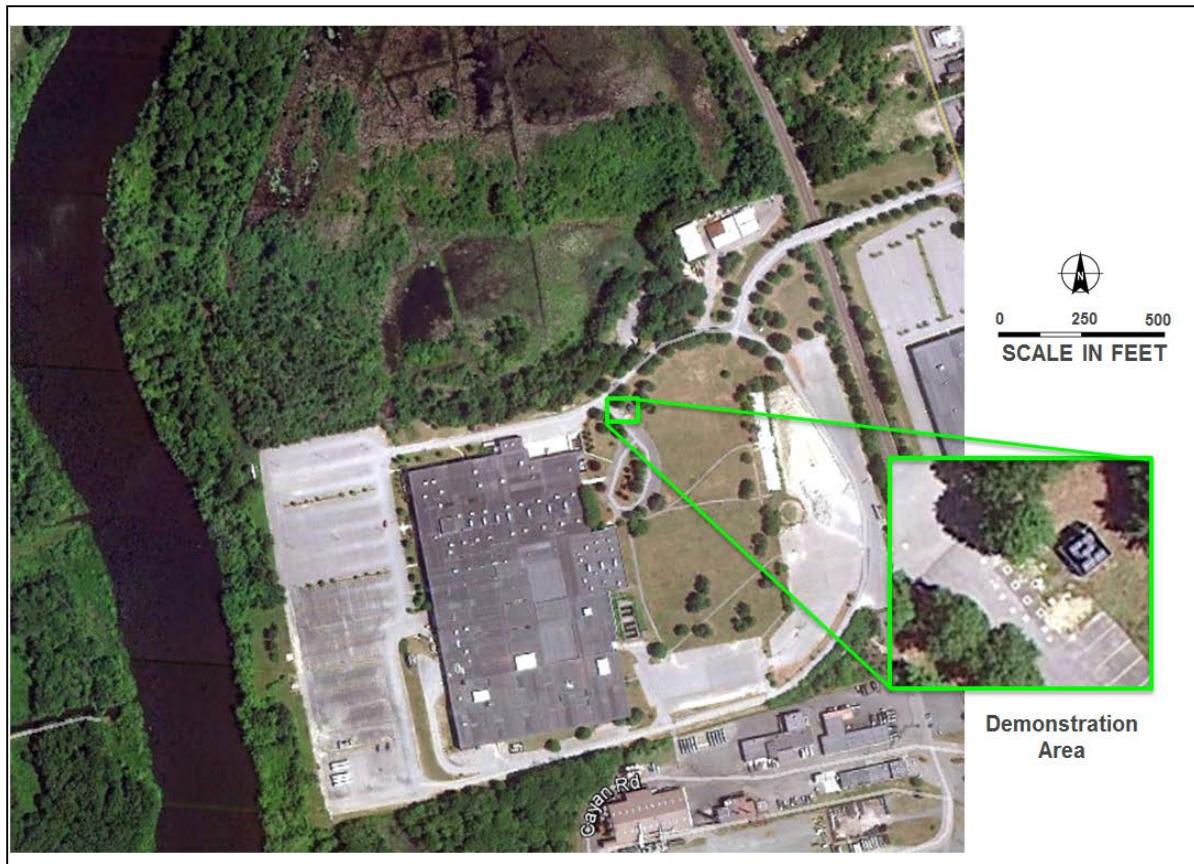
Figure 3. Demonstration Area

4.2   SITE GEOLOGY/HYDROGEOLOGY

Site documents indicate localized geology in the demonstration area can be generally classified as stratified layers of fine sand and silt with few clay layers. A silt layer was penetrated consistently at a depth of about 45 feet below ground surface (bgs), which is consistent with other areas of the larger Site (GZA, 2011). Groundwater was encountered at a depth of approximately 20 feet bgs in the demonstration area. Based on potentiometric surface maps, groundwater flow in the vicinity of the demonstration area is to the northwest (GZA, 2011). In other portions of the Site, groundwater flow is more westerly, towards a river located west of the Site. A cross-section through the demonstration area, including the positions of the well-screens used for DNAPL recovery, is shown in **Figure 4**.
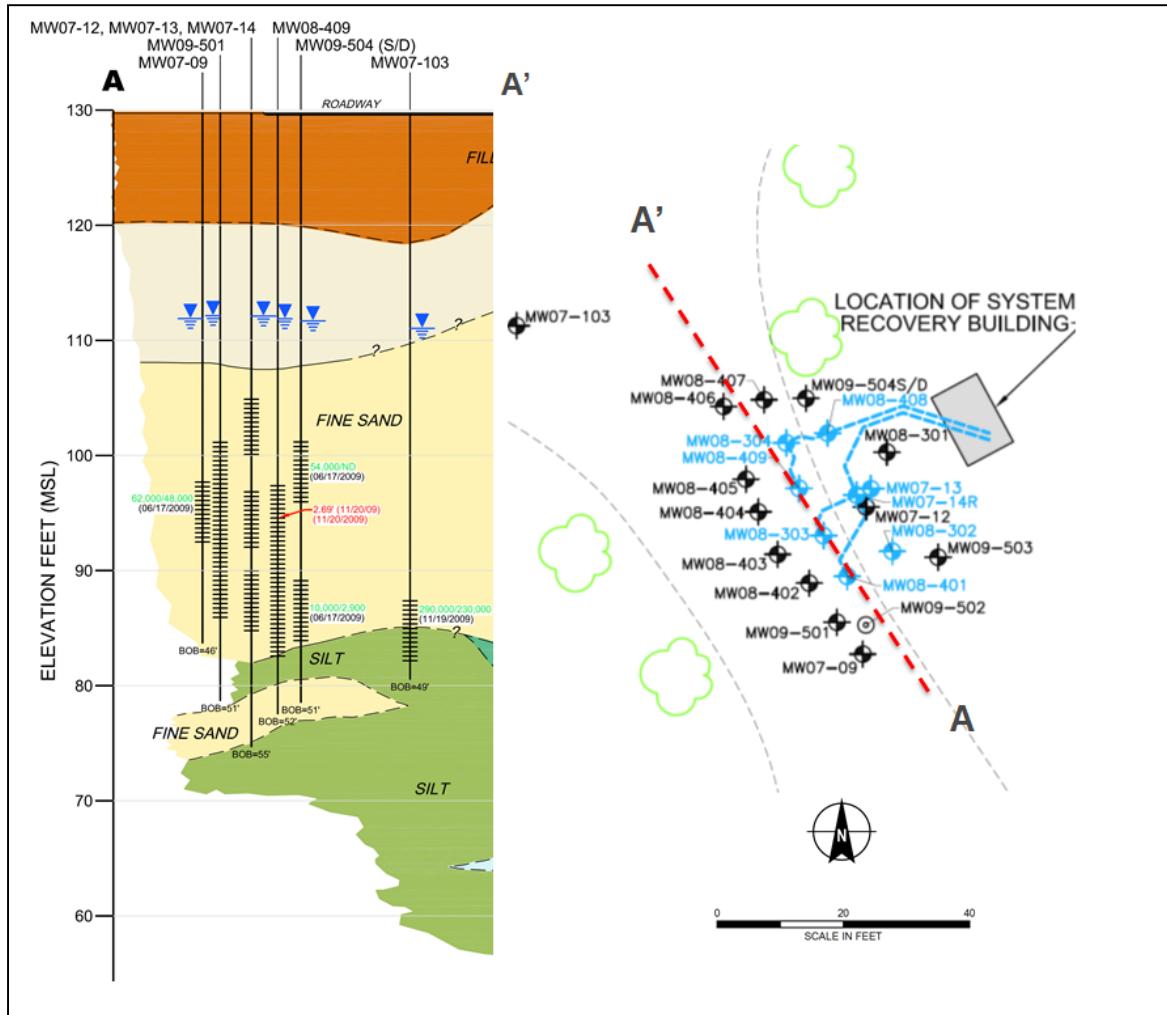
Figure 4. Cross-Section through Demonstration Area (from GZA, 2011). Wells with Current or Historical DNAPL Occurrence are Shown as Blue.

4.3 DNAPL OCCURRENCE

DNAPL recovery wells were installed in the planned demonstration area from 2007 to 2009. The well locations are shown in **Figure 4**. The recovery wells are generally screened from 30 to 45 feet bgs. The selection of the screen depth intervals was based on visual evidence of DNAPL in soil cores at depths ranging from 35 to 45 feet bgs (GZA, 2011).

The recovery system had recovered 338 gallons as of December 2010 (GZA, 2011). Historically, the majority of DNAPL has been recovered from wells MW08-303, MW08-304, MW08-401, and MW07-14R. Other wells (MW07-13, MW08-32, MW08-408, and MW08-409) have had sporadic occurrences of DNAPL; however, DNAPL has not been observed recently in those wells (GZA, 2011).

4.4   OTHER HIGH RESOLUTION SITE CHARACTERIZATION DATA SETS

In addition to DNAPL recovery data, other HRSC data is available for the Demonstration Area, including MIP and Waterloo Profiler borings. The MIP tool was described previously in Section 1.1. The Waterloo Profiler is a tool used for collecting multiple groundwater samples at different depths from the same DP boring. The version of the Waterloo Profiler used at the Site was Stone Environmental's Waterloo[APS]. The tool works by injecting a steady stream of water into the sub-surface as the tool is advanced (Pitkin et al., 1999). This helps prevent clogging of the sampling screen with sediments and also provides high-resolution information on the hydraulic properties of the formation. It does this by continuous monitoring of pressures and injection rates providing a parameter referred to as index of hydraulic conductivity (I_k). When a target depth interval for groundwater sampling is reached, the water flow is reversed and a groundwater sample is collected. This is after sufficient purging has happened to ensure the water pumped is representative of formation groundwater, which is also verified via monitoring/stabilization of various parameters with a multi-parameter probe while purging.

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5.0   TEST DESIGN

5.1   CONCEPTUAL EXPERIMENTAL DESIGN

The field demonstration included two components. The first component was completed during the first week and included a grid of closely-spaced DyeLIF probes advanced in the suspected DNAPL source area. The second component, completed during the second week, included high-resolution vertical sampling of soil cores collected from soil borings advanced adjacent to select DyeLIF probes.

5.2   BASELINE CHARACTERIZATION ACTIVITIES

No intrusive baseline characterization activities were completed for the field demonstration. As described above, a number of closely-spaced DNAPL recovery wells are located in the demonstration area. In addition, a number of soil borings, MIP probes, and groundwater profiling data were available for the demonstration area from prior investigations. This data provided adequate baseline characterization for the subsequent DyeLIF probing.

5.3   FIELD TESTING

As described above, the field demonstration included two components, one week of DyeLIF probing and a second week of follow-on soil coring. The DyeLIF program is described in Section 5.3.1; the follow-on soil coring is described in Section 5.3.2. DP drilling services for both weeks were provided by Stone Environmental using a Geoprobe 7822 rig. A second Geoprobe rig from Dakota was onsite and completed a portion of the DyeLIF probing the first week while the other Geoprobe rig from Stone performed the re-entry grouting.

5.3.1   DyeLIF Probes

DyeLIF probes were advanced throughout the suspected DNAPL source area the week of October 7, 2013. Probes were advanced to a depth of approximately 70 feet bgs. This depth was selected based on available characterization data for the suspected DNAPL source area, which indicated DNAPL potentially extended down to this depth interval.[7] DyeLIF probe locations are shown in **Figure 5**. A "DL-XX" naming convention was used for the DyeLIF probes, e.g., the first DyeLIF probe advance was denoted as "DL-01." In certain locations, duplicate DyeLIF probes were advanced next to the original DyeLIF probe.[8] Because the duplicate probes were only approximately 1 foot away from the original probes, they are not shown in **Figure 5** in order to improve the readability of the figure.

(Figure 12 from Final Report)

Figure 5. DyeLIF Probe and Soil Boring Locations

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[7] Data indicating the likely maximum depth of DNAPL in the source area consisted of depth-discrete groundwater samples from a downgradient sampling transect. Results from the DyeLIF study confirmed the initial prediction of maximum DNAPL depth obtained from the downgradient HRSC transect, validating the "transect approach."
[8] Duplicate in the sense that the "duplicate" boring was advanced adjacent to the original DyeLIF boring.

A second, shorter DyeLIF investigation was completed March 15–17, 2014. This investigation included the advancement of 11 CPT probes to depths of approximately 70 feet bgs. The objective of the mobilization was to test the new CPT version of the DyeLIF, and this event did not include the detailed soil sampling that was a component of the larger two-week field study completed in 2013.

5.3.2   Co-located Soil Borings

During the second week of the field demonstration, a Geoprobe rig was used to advance closed-piston soil samplers adjacent to select DyeLIF probes that had indicated DNAPL was present at a particular location. Continuous soil cores were collected across the suspected DNAPL depth interval, – i.e., cores were collected beginning at a depth several feet above the suspected DNAPL interval and were then collected continuously to a depth several feet below the suspected DNAPL zone. There were two objectives for the soil boring program. The first was to qualitatively compare the inferred in-situ DNAPL distribution from Dye-LIF probing with high-resolution soil sampling in a co-located soil boring. The second objective was to collect soils that had a wide range of DNAPL pore saturations for aboveground analysis. Those samples ranged from soils with no DNAPL to soils most heavily impacted by DNAPL with the highest documented saturations at the site (based on DyeLIF responses).

The strong spatial variability in the occurrence and saturation of residual DNAPL in the subsurface makes it difficult to quantitatively compare results from a DyeLIF probe to data (chemical data or visual tests using hydrophobic dyes) collected from nearby borings. Because of the expected variability in the distribution of residual NAPL, it is not reasonable to expect that NAPL will occur at the same depths and concentration/saturation in borings located even 1 foot away. Early field demonstrations of LIF technologies in the 1990s relied on this type of "verification" but, not surprisingly, often found poor correlation between LIF responses and data from soil samples collected from borings drilled just a few feet away.

To reduce (but not eliminate) biases resulting from the heterogeneous distribution of DNAPL in the subsurface, replicate samples for various types of testing were collected from the same depth interval from within the same soil core. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with tabletop DyeLIF, the second was field-preserved in methanol for subsequent laboratory analysis; the third was collected for moisture content analysis, and a fourth sub-core underwent a dye "shake test" using a visual hydrophobic dye (Oil-Red-O). Photoionization Detector (PID) readings were also collected at each depth interval. The sub-core data was used for quantitatively evaluating the performance metrics described in Section 3.0. More details on the coring and sub-sampling methods are included in Section 5.3.3.

A total of eight borings were advanced adjacent to selected DyeLIF probes. The core hole/sample identifications for the borings in the data summary tables in the Final Report are denoted by the DyeLIF boring was co-located with the soil boring. For example, a soil boring advanced adjacent to DL-27 would be denoted with the same designation of "DL-27." In some locations, more than one co-located soil boring was advanced next to the original DyeLIF location. This was done primarily to try different coring methods in an attempt to improve soil core recovery. For example, three co-located soil borings were advanced next to DL-23. The letter A, B, and C were used to denote successive co-located borings. For example, at DL-23, the three co-located are denoted as "DL-23A," "DL-23B," and "DL-23C." Because the soil borings were only approximately 1 foot away from the original DyeLIF borings, they are not shown in **Figure 5** in order to improve the readability of the figure.

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5.4   SOIL SAMPLING METHODS

Achieving a high percentage of core recovery during the soil sampling portion of the field demonstration proved difficult due to the fine sands and soft silts at the site. Different coring methods, run lengths, and operating variables were attempted in an effort to improve recovery. The best recovery was achieved using a modified version of the Geoprobe Macro-Core (MC7™) sampler, which provides 3-inch diameter cores.[9] The MC7 tool was adapted to include a sealed piston above the soil core, which was tied off in a fixed position while the core barrel was advanced through the target core interval (method adapted from Zapico et al., 1987) with the goal of providing higher recovery and retention of pore fluids. Run lengths of 3 feet were used based on initial trials to maximize recovery. However, recovery still only ranged from about 50% to 85%, with an average of 65%. Part of the reason for lower recovery was the smaller diameter cutting shoe (~68 millimeters [mm]) versus the sample tube diameter (~75 mm), such that the soft sediments expanded out in the larger tube length and compressed accordingly (under these conditions the maximum recovery expected is about 83%). Based on this, a correction factor was applied to convert sub-sample positions in the core tubes to inferred in-situ depths.

As described in Section 5.3.2, to reduce (but not eliminate) biases resulting from the heterogeneous distribution of DNAPL in the subsurface, replicate samples for various types of testing were collected from the same depth interval from within the same soil core. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with tabletop DyeLIF, a second was field-preserved in methanol for subsequent laboratory analysis, a third was collected for moisture content analysis, and a fourth sub-core underwent a dye "shake test" using a visual hydrophobic dye (Oil-Red-O). PID readings were also collected at each depth interval. Appendix B of the Final Report includes a series of photos that depict the sub-coring and sampling process, as well as additional information on the calibration of analytical equipment, quality assurance sampling, decontamination procedures, and grouting methods used for the DyeLIF and soil borings.

5.5   SAMPLING RESULTS

5.5.1   DyeLIF Results

Three types of data products were generated in the field from the DyeLIF data. The first data product is the raw DyeLIF log. That log depicts the total response verses depth. The raw DyeLIF logs also depict the flow rate of the dye solution and the measured backpressure. The raw DyeLIF logs are included as Appendix C of the Final Report.

The second data product is an Advanced Data Analysis (ADA)[10] multi-panel plot that shows the raw waveform to the far left and then various waveforms that contribute to the overall fluorescence to the right. For the field demonstration, these waveforms included internal instrument background, non-solvated dye, sand, and DNAPL. This graphic facilitates field analysis of the types of fluorescence contributing the most total fluorescence and helps to identify smaller DNAPL-generated fluorescence peaks that might otherwise be lost in a plot showing just the total fluorescence. The multi-panel plots depicting the results of the ADA are included as Appendix D in the Final Report.

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[9] The larger core diameters were required in order to collect multiple sub-cores at the same depth interval.
[10] Refer to the Final Report for additional information on the ADA process.

The third data product produced from the DyeLIF data is the multi-panel DNAPL plot. This graphic plots 5-foot increments of the DNAPL waveform plot on the same printout, which facilitates identification of thinner DNAPL layers. These plots can be extremely useful when probing into deeper depths where a single panel would not provide adequate resolution. The multi-panel DNAPL plots are included as Appendix E in the Final Report.

5.5.2   Soil Sampling Results

Table 3 of the Final Report summarizes the soil coring program. The table includes fields for boring location, the sampling method,[11] the sampling depths in feet bgs, the total sampling interval length in feet, the percent recovery achieved, and the number of sub-core intervals within each soil core. A total of 260 depth intervals were sampled.

Table 4 of the Final Report summarizes the sub-coring sampling results. The table includes a unique sample identification number for each sub-core sampling interval and additional fields for boring location, sample depth, VOC sampling results,[12] estimated DNAPL saturation,[13] Oil-Red-O dye shake test results, tabletop DyeLIF testing, and PID screening results.

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[11] As described in previous sections, three different coring methods were attempted in an effort to determine which method yielded the best recovery.

[12] 133 of 260 sub-core sampling intervals were submitted for laboratory analysis of VOCs.

[13] DNAPL saturations were estimated from laboratory analytical results using the software NAPLANAL. The NAPLANAL code uses equilibrium partitioning theory to estimate DNAPL saturations.

6.0   PERFORMANCE ASSESSMENT

6.1   CORRELATION BETWEEN SUB-CORES

The performance objective for chemical analysis was 70% consistency between positive DyeLIF responses and samples when laboratory results indicated DNAPL saturations > 5%. The demonstration results showed 100% consistency between chemical analysis and DyeLIF for saturations down to 1.9% (35 of 35 samples), and 95% consistency for estimated saturations > 0.5% (40 of 42 samples). Therefore, the performance objective for chemical analysis was exceeded.

The performance objective for the dye shake tests was 70% consistency between a positive DyeLIF response and a positive colorimetric response with the dye shake test when the DNAPL saturation was estimated to be > 5%. For the dye shake tests, the demonstration results showed 100% consistency between DyeLIF and the shake tests at saturations down to 1.3% (37 of 37 samples).[14] There was 98% consistency between DyeLIF and dye shake tests when saturations were > 0.5% (41 of 42 samples). Therefore, the performance objective for dye shake tests was exceeded.

One issue identified during the field program was that at low saturations the DNAPL would sometimes separate out of the sand and cling to the glass in the upper portions of the vial. This proved problematic for the tabletop DyeLIF testing as the protocol used was to place the bottom of the sample vial on the laser window and rotate it while readings were collected. This resulted in LIF readings being taken in the soil rather than on the glass sidewalls where the DNAPL had preferentially accumulated. Greater consistency at low saturations (<0.5%) would have likely been achieved by reading the glass sidewalls with DyeLIF rather than the soil at the bottom of the glass vials (making it equivalent to visual dye methods where detections are enhanced by preferential adherence of the red-colored DNAPL to the sidewalls). Therefore, while this testing indicated a detection limit of around 0.5% saturation, the detection limit in-situ is likely even lower.

6.2   TOOL DURABILITY AND PRODUCTION RATE

The hammering and stress of percussive drilling over the one week drilling program allowed the project team to evaluate the durability of the DyeLIF tool. A performance objective of 90% uptime was the specified goal in the work plan for the field demonstration. A performance objective was also established for the average linear feet of drilling production achieved per day. A performance goal of 150 feet per day was proposed in the work plan.

In the field demonstration, 100% uptime was achieved by having a second set of downhole tooling (DyeLIF sub and probe rods pre-strung with DyeLIF cables) available that could be utilized in the event that minor maintenance of the first set of downhole tooling was required. This approach is also used by most MIP contractors as a way to prevent project downtime while repairs to the MIP system are made. During the weeklong field event, the downhole tooling had to be swapped out one time when the DyeLIF encountered a minor issue requiring repair.[15]

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[14] For one of the samples, both the DyeLIF test and the dye shake test indicated no DNAPL was present. Therefore, the samples were consistent with each other but contradicted in the laboratory data. This data suggests that there may have been some intra-core heterogeneity.

[15] This repair required approximately one hour. Therefore, if the second set of tooling had not been onsite, the uptime would have still been close to 100%.

The production rate for the week of DyeLIF probing averaged > 400 feet of probing per day, greatly exceeding the 150-feet-per-day goal. The production rate was helped by a second rig on-site that was performing some of the re-entry grouting. This approach limited any downtime of the DyeLIF rig during grouting. It is estimated that the production rate would have decreased approximately 20% if the DyeLIF rig also performed the re-entry grouting. Dakota has maintained a running average production rate for its TarGOST LIF tool over many years and dozens of sites probed at 334 feet per day. A 20% reduction in the achieved production rate would have been consistent with the running TarGOST average of 334 feet per day.

The production rate, coupled with the extremely fine vertical resolution of DyeLIF (~ 1 data point per 0.5 cm probed) is a result of the extremely high data acquisition rate of the DyeLIF tool. Using the running TarGOST production rate average of 334 feet probed per day, the number of data points generated per day would be >20,000. Considering the excellent correlation between DyeLIF and colorimetric dye shake tests, one day of DyeLIF probing is essentially equivalent to conducting 20,000 colorimetric dye shake tests, something that would take several months of soil coring and detailed sub-coring to complete.

6.3   NO DRAG-DOWN OF DNAPL

No drag-down of DNAPL was observed in the DyeLIF logs. This is consistent with the thousands of LIF probes advanced in NAPL sources by Dakota. The absence of drag-down in this project or other LIF NAPL investigations is primarily because CPT and other DP tools displace 100% of the volume of the DP probe, creating a seal against the DP rods and tooling as they are being advanced. This can be contrasted with soil borings, where the soil is physically removed from the subsurface, thereby increasing the potential for vertical migration of DNAPL.

The concern of vertical migration is further mitigated by employing appropriate grouting techniques either retraction or re-entry grouting. For the field demonstration, re-entry grouting was used. This involves reentering the hole with DP rods equipped with a sacrificial tip.[16] Once the depth of the previous boring was reached, the rods were retracted, causing the sacrificial tip to dislodge. Grout was then pumped into the rods as they were retracted, analogous to a tremie pipe. Retraction grouting and "grouting while advancing" techniques have also been demonstrated for DP applications (Lutenegger and DeGroot, 1995).

6.4   3D GRAPHICAL DEPICTION OF DNAPL SOURCE ZONE

The data acquisition rates and vertical resolution of the DyeLIF generates high-resolution datasets that can be used for 3D rendering of chlorinated solvent DNAPL source zones at a resolution and accuracy previously not possible with conventional technologies and approaches. 3D renderings of the actual DNAPL source zone at the demonstration site are shown in **Figure 6**.

As shown in **Figure 6**, the majority of the DNAPL at the field demonstration site is located at approximately 35 feet bgs, with smaller intervals of DNAPL located at deeper depths.

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[16] The DyeLIF rods are pre-strung with the dye injection tubing and the LIF cables. A separate set of rods that are not pre-strung with the DyeLIF cables were used for grouting purposes.

The 3D rendering of the DNAPL source zone is consistent with laboratory experiments (Christ et al., 2010; Fure et al., 2006; Kaye et al., 2008; Oostrom et al., 1999) and numerical modeling (Basu et al., 2008; Christ et al., 2005; Lemke et al., 2004; Park and Parker, 2005) of DNAPL migration, which has demonstrated that DNAPL tends to pool and migrate laterally when encountering permeability changes.

The authors of this study suggest that the 3D depictions of DNAPL in **Figure 6** constitute the most detailed and accurate definition of subsurface DNAPL ever obtained at a field site. This level of DNAPL delineation is clearly invaluable for optimizing source zone remediation efforts.
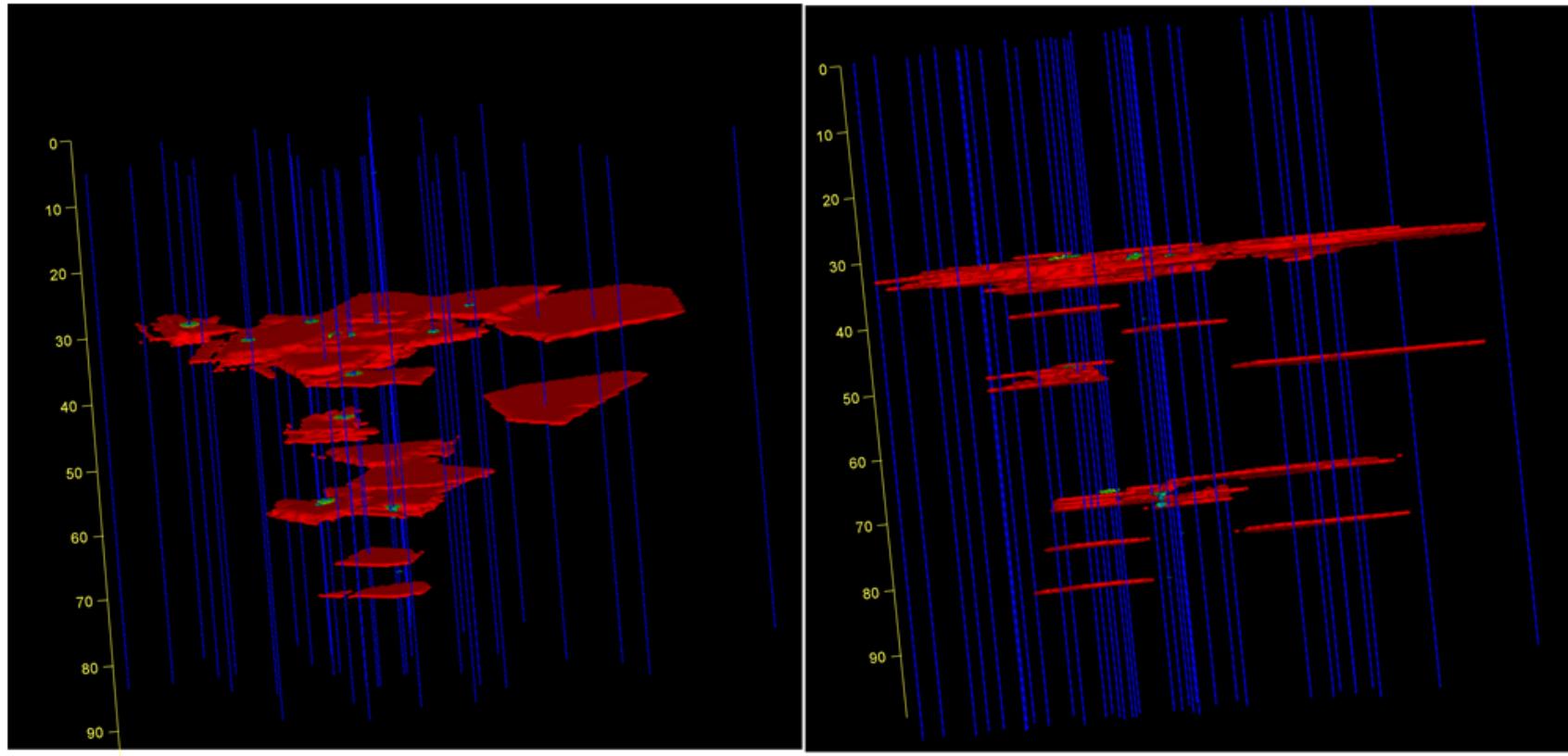
Figure 6. 3D Graphical Depiction of DNAPL Source Zone at Demonstration Site.

7.0   COST ASSESSMENT

7.1   COST MODEL

The cost model for the DyeLIF tool is straightforward and includes two components. The first component is the daily rate for DyeLIF. Based on the success of this demonstration project, Dakota began to offer the DyeLIF tool commercially in summer 2014. DyeLIF currently is offered from Dakota for a rate of $3,500/day. This includes the DyeLIF equipment and an operator from Dakota to operate the DyeLIF system. Dakota's equipment and services are typically used in conjunction with a Geoprobe or CPT rig that is retained locally. While Dakota can provide Geoprobe services for projects located within driving distance from Fargo, North Dakota, it is more common for Dakota to ship the DyeLIF (or TarGOST) equipment to a given project site and rely on a local DP contractor to provide Geoprobe or CPT services. For the cost model, it is assumed that a local DP rig is provided at a cost of $1,500/day such that the total cost for the DyeLIF equipment and the DP rig is $5,000/day. Mobilization costs for DyeLIF range from $3,500 to $4,000, depending on logistical challenges. This includes the travel for the DyeLIF operator.

The second component of the cost model is an assumed daily production rate. As described in previous sections, Dakota maintains a long-term running average production rate for the TarGOST tool. The current running average production rate is approximately 334 feet per day of probing. In the demonstration study, the average production rate exceeded 400 lineal feet of probing per day. This number was inflated somewhat, however, given that a second rig was used for some of the grouting work. For cost-estimating purposes, a number of 325 feet per day was selected as a more appropriate production rate assuming one rig does both probing and grouting.

To estimate the cost for a DyeLIF investigation, divide the total lineal feet of estimated probing by the assumed production rate to determine the estimated number of days required to complete the DyeLIF investigation. Note that this cost does not include oversight from the site consultant, mobilization fees, utility clearance for probing locations, and any reclamation work required to repair probed locations.[17] Because Dakota has the ability to email the DyeLIF logs to the project team after each push, a single onsite field person from the site consultant's firm is appropriate.

7.2   COST DRIVERS

The primary cost driver for a DyeLIF investigation is the area and depth of the investigation. In the Final Report, the use of near-source transects of MIP probes or groundwater profiling to map high-concentration plume cores is discussed. Mapping high-concentration plume cores helps define the lateral (perpendicular to groundwater flow) and vertical dimensions of the suspected DNAPL zone that can then be targeted for the DyeLIF investigation. This preliminary step will typically greatly reduce the area and depth of the investigation.

Another cost driver is the spacing of the DyeLIF probes. Because of the complexity of most chlorinated solvent DNAPL source zones, probing offsets on the order of 10 -20 feet for most sites is recommended (i.e., is not recommend increasing probing offsets in order to decrease the total amount of probing).

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[17] A more detailed estimate that includes mobilization, per diem, and consultant oversite is included in Section 7.3.

7.3 COST ANALYSIS

The technology most comparable to the DyeLIF technology is high-resolution soil sampling and subsequent field screening using dye shake tests. Sub-cores could also be analyzed via an onsite lab with high-throughput chemical analysis (e.g., Direct Sampling Ion Trap Mass Spectrometer [DSITMS]). As described in previous sections, field screening with dye shake tests was performed during the second week of the field demonstration and correlated extremely well with DNAPL-impacted intervals.

While the effectiveness of simple dye shake tests and the use of onsite laboratories with high-throughput sample analyses makes high-resolution vertical sampling of continuous cores feasible, there is still a large amount of labor required to collect soil samples at such a high vertical resolution. This limits the overall production rate (i.e., linear feet drilled and sampled per day) that can be achieved. During the field demonstration for example, 121.5 feet of coring was completed over 4.5 days of drilling (average of 27 feet/day). Total core recovery was 70.9 feet (average of 16 feet/day). The production rate was limited somewhat due to experimentation with different coring methods in an attempt to improve core recovery. Therefore, the average production rate during the field demonstration is likely an underestimate of what could typically be achieved per day. However, even doubling the production to approximately 50 feet/day is still significantly less than the production rate achieved with the DyeLIF tool.

A cost comparison of high-resolution soil sampling and DyeLIF is included in **Table 2**. It is assumed that a closed-piston, large-diameter soil sampler (e.g., Geoprobe MC7) would be utilized to provide greater core recovery and enough sample volume to collect multiple samples at each depth interval. It is assumed that PID screening would be completed every 0.167 feet (~5 cm) and that 25% of the PID locations (75 total samples) would undergo dye shake tests analyzed at the onsite laboratory. As shown in **Table 2**, due to the higher production rate and higher vertical resolution of the DyeLIF, the costs per data point are significantly lower. The costs per data point for DyeLIF, dye shake test, and onsite laboratory are $0.40, $58.67, and $98.67 per data point, respectively.

Table 2. Cost Comparison of DyeLIF and High-Resolution Soil Sampling.

DyeLIF	High Resolution Soil Sampling (50 feet/day assumption)[a]
Costs: • DyeLIF: $3,500 • Mobilization: $700[b] • DyeLIF operator per diem: $150 • Geoprobe rig: $1,500 • Mobilization: $100[3] • Geoprobe operator per diem (2 persons @ $150/day): $300 • Consultant field staff (1 person, 10 hours @ $100/hour): $1,000 **Total Cost:** $7,250	**Costs:** • Geoprobe rig: $1,500 • Mobilization: $100[c] • Geoprobe operator per diems (2 persons @ $150/day): $300 • Consultant field staff (2 persons, 10 hours @ $100/hour): $2,000 • Consultant field supplies (VOA vials/equipment): $500 • Onsite laboratory:[a] $3,000 **Total Costs Without lab:** $4,400 **Total Cost With Lab:** $7,400
Production Rate: • 300 feet of probing per day • Vertical sampling resolution: 0.5 cm • Total data points generated per day (300 feet/0.5 cm): 18,288 data points per day	**Production Rate:** • 50 feet of probing per day • Vertical PID screening resolution: 0.167 feet (~5 cm) • Total PID screening locations: 300 • Total dye shake and lab samples @ 25%: 75
Cost per Data Point: • $7,250/18,288 = $0.40/data point	**Cost per Data Point:** • Dye shake test: $4,400/75 = $58.67/data point • Onsite lab sample: $7,400/75 = $98.67/sample

Notes:
a. Assumes high-throughput onsite lab that can process around 80 samples per day.
b. Assumes mobilization costs of $3,500 spread out over 5 day event.
c. Assumes $500 mobilization fee spread out over 5 days.

Another cost that is important to consider is the impact that a DyeLIF investigation would have on remediation costs. More accurate mapping of the DNAPL source zone allows for much more targeted and focused source zone remediation, particularly if in-situ remedial options such as chemical oxidation or thermal treatment are selected (Kueper et al., 2014; Stroo et al., 2012). As described in Section 1.1, a major limitation of the MIP tool and groundwater profiling is the inability to distinguish NAPL from high-concentration dissolved/absorbed phase contamination. This limitation is particularly important when considering our improved understanding of dissolved-phase plume morphology downgradient of DNAPL source zones. Early conceptualizations of dissolved phase plumes predicted that there would be large amounts of homogenization and mixing as contaminants migrated downgradient away from the DNAPL source. However, studies that have employed high-resolution characterization of the dissolved phase plume along one or more transects oriented perpendicular to the groundwater flow direction have shown that hydrodynamic dispersion (mixing) is much less than was originally assumed, and high concentration plume cores can maintain their strength and structure over relatively long travel distances (Einarson et al., 2010; Guilbeault et al., 2005).The implication of this in relation to characterization of DNAPL source zones with MIP or groundwater profiling is that the DNAPL source zone and inferred mass of DNAPL could appear much larger than they actually are because (1) high-concentrations typically extend well downgradient of the residual DNAPL due to limited mixing and (2) MIP/groundwater profiling is unable to differentiate between DNAPL and high concentration dissolved-phase VOCs.

This limitation of MIP and groundwater profiling in terms of DNAPL delineation was apparent at the field demonstration site. Two transects of MIP probes were advanced downgradient of the DNAPL source several years prior to the DyeLIF investigation. The Electron Capture Detector (the detector specific to chlorinated compounds in the MIP) maxed out along both transects at horizontal and vertical depth intervals corresponding to up-gradient DNAPL. MIP probes MIP-114 and MIP-210 along the first transect and MIP-115, MIP-155, MIP-158, and MIP-159 along the second transect all maxed out (**Figure 7**). In addition, a depth-discrete groundwater sample exceeded 10 milligrams per liter of TCE (>1% of solubility, suggesting DNAPL presence) along this second transect. The DNAPL source delineated using DyeLIF was only approximately 15 feet parallel to flow by 45 feet perpendicular to flow in plan-view (**Figure 7**). The second MIP/groundwater sampling transect was approximately 100-feet downgradient of the edge of the DNAPL source. This illustrates how, when using the MIP tool, the DNAPL source zone could be misconstrued as being much larger than it actually is. Therefore, in addition to the investigation on cost savings, there is the potential for large remediation cost savings. This can be done by focusing DNAPL source remediation on only the portions of the subsurface that actually contain DNAPL.
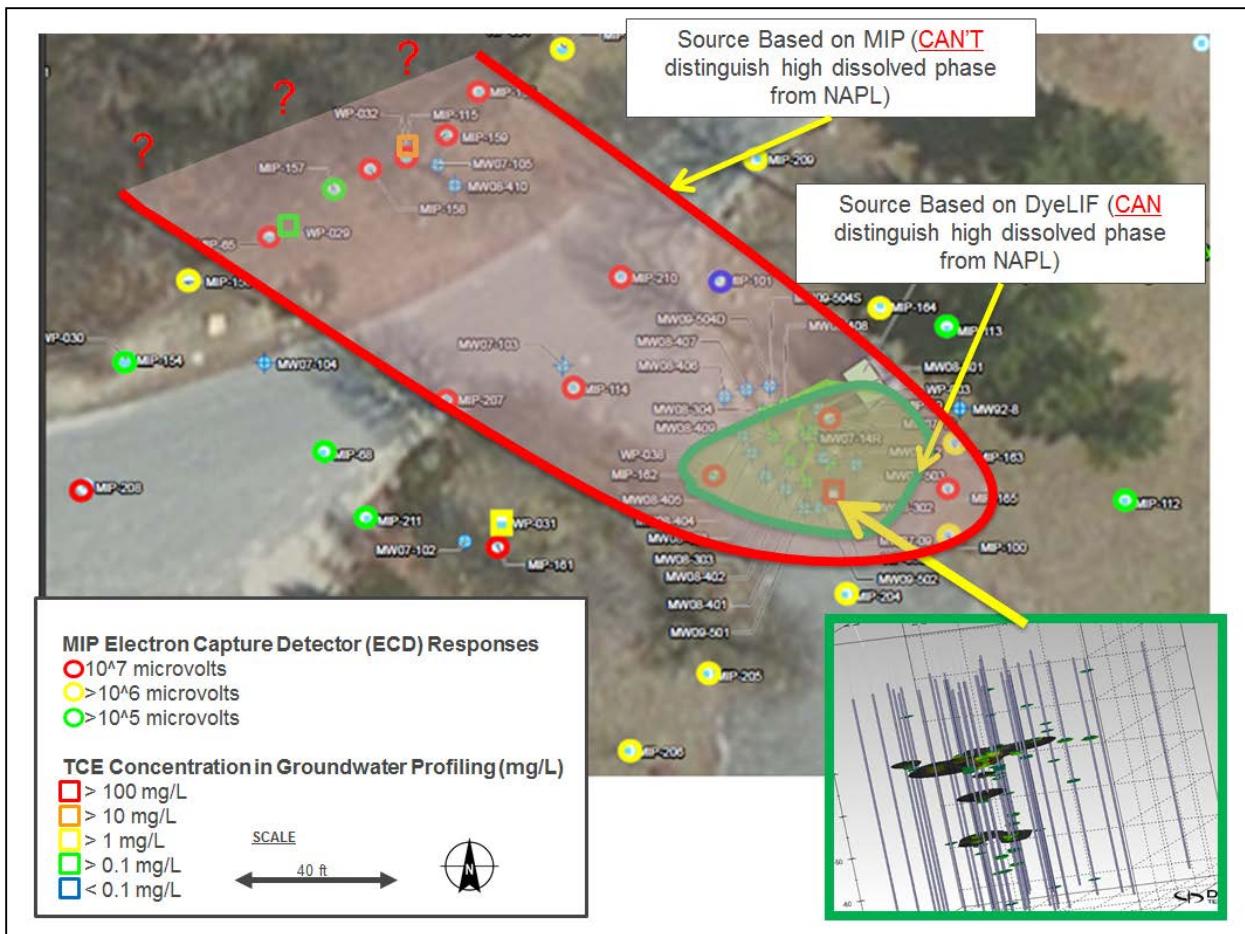
Figure 7. Comparisons of DNAPL Source Zone Delineation Using DyeLIF and MIP with Depth-Discrete Groundwater Sampling.

While this section has described some of the limitations of MIP and high-resolution soil sampling related to DNAPL source zone investigation, it is noted that these tools are complementary to the DyeLIF technology if utilized correctly. For example, mapping the high-concentration dissolved-phase plume cores downgradient of DNAPL source zones can result in a more focused DNAPL investigation using DyeLIF. Because of the limited mixing of the dissolved-phase plume that occurs downgradient of the DNAPL, a near-source transect of MIP probes or high resolution groundwater sampling using profiler tools (e.g., Waterloo APS™) helps to define the approximate width (i.e., perpendicular to flow) and vertical extent of the DNAPL source zone.

Once the DNAPL source zone has been mapped with DyeLIF, targeted soil sampling can be used to evaluate DNAPL composition and other properties. High-resolution soil sampling can also be used to evaluate the extent that dissolved-phase VOCs have penetrated into adjacent low permeability zones and could serve as a source of back-diffusion following source zone treatment (Adamson et al., 2015; Chapman and Parker, 2005; Parker et al., 2004). The integration of these different high-resolution tools is described in the following section, 8.0.

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The authors of this report believe that the new DyeLIF technology will be a "game-changer" for characterizing DNAPL sites in the United States and around the world. There are many examples where source zone remediation has been performed, only for it to be discovered later that only a portion of the residual DNAPL was removed or treated. In response, many remediation system designers now err on the side of conservatism and overdesign source zone remediation systems. The additional and ongoing costs of ineffective and overly conservative source zone remediation are staggering. EPA estimates that $209B is needed to fully remediate hazardous waste sites in the United States (USEPA, 2004). An expert panel with the National Research Council (NRC) considers that figure an underestimate of the actual costs that will be incurred, partially because the distribution of the areas contaminated remains undefined (National Research Council, 2013). The NRC authors stress that improvement of long-term management of hazardous waste sites requires a much better understanding of the spatial distribution of the contaminants in the subsurface, which can be obtained by the application of emerging diagnostic tools (e.g., DyeLIF). Thus, development and application of the new DyeLIF technology would quickly and fully delineate subsurface DNAPL in 3D and will likely be a game-changing new site assessment technology that will lead to much more focused and effective source zone remediation programs.

8.0   IMPLEMENTATION ISSUES

No major implementation issues were identified during the field demonstration. However, a key limitation for any DP technology is suitability of the geological conditions for DP probing, i.e., absence of cobbles or other conditions that would cause tool damage and preclude advancing the probes. A frequently asked question about the dye concerns the potential for regulatory resistance to the technology because of the injection of dye as the probe is advanced into the subsurface. The project team does not anticipate regulatory resistance to the technology based on the following:

- The dye is relatively non-toxic (Rat LD50 [intraperitoneal] 4170 mg/kg) and is not a known or suspected carcinogen. From a toxicity standpoint, the dye is therefore similar to fluorescent groundwater tracing dyes that are released in much greater quantities during tracer studies.

- A de minimis quantity of dye is injected (only 0.11 grams per meter of probe penetration).

- Analytical testing on water left in contact with the dye for several days yielded no detectable levels of any listed VOCs or semi-VOCs.

- The dye is extremely hydrophobic and, therefore, it is expected that there is very little transport of the dye in groundwater away from the probed location.

- Because the DyeLIF tool is used to assess DNAPL in the subsurface, the dye is being injected at a de minimis quantity into a portion of the subsurface that is already heavily impacted by chemicals that are toxic and carcinogenic.

Another potential issue evaluated was that in plastic soils (e.g., stiff clays) there is potential for the thickness of the dye interaction zone to increase to approximately 1-2 mm. Intuition suggests that this thicker layer of dye solution might interfere with sensing of DNAPL globules located in the soil on the far side of the dye layer that is in contact with the soil. Laboratory studies performed at Dakota's facility to investigate this potential issue show that the indicator dye fluid is fairly transparent to the DyeLIF's excitation laser beam. In laboratory tests with a 2 mm-thick layer of dye solution, there was only a modest (~15%) loss in fluorescence measured at the back of the dye layer versus the dye in direct contact with the sapphire window (no fluid layer).

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9.0   REFERENCES

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